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Temperature Factors and Thermodynamic Properties of Crystals

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Temperature factors and thermodynamic properties of crystals can be related easily and practically by use of the quasi-harmonic description of lattice vibrations. The explicit introduction of particular forms of frequency distributions or force-constant models is not required.

For cubic crystals containing one type of atom, temperature factors can usually be obtained more accurately from thermodynamic data than from scattering measurements. For more complicated structures containing different kinds of atoms, the thermodynamic data are related to a linear combination of temperature factors.

1. Introduction

Temperature factors enter explicitly into all structure analyses made by diffraction methods. They are commonly defined (Lipson & Cochran, 1953) through the scattering factor

$$f=f_0 \exp(-B \sin^2 \theta/\lambda^2)\,, \tag{1.1}$$

where f_0 is the atomic scattering factor, B the temperature factor, θ the Bragg angle and λ the wavelength of the incident radiation. Alternatively, B may be expressed by

$$B=8\pi^2\overline{u^2}\,, \tag{1.2}$$

where $\overline{u^2}$ is the mean square displacement, perpendicular to the reflecting plane, of an atom due to its vibrational motion. Physically, the lattice vibrations modify local electron density distributions, reducing the Fourier components which give rise to Bragg reflexions and adding a continuous spectrum of Fourier components which do not have the periodicity of the crystal lattice. The reduction of the Bragg intensities depends upon the amplitude of the vibrations [equation (1.2)] and so is temperature dependent. Temperature factors are sometimes estimated empirically (Lipson & Cochran, 1953) but more often they are evaluated as parameters of a structure analysis.

In more general terms, the temperature dependence of Bragg reflexions is called the Debye–Waller effect (Debye, 1914; Waller, 1925). It is convenient for our purposes to discuss the Debye–Waller factor, M, which is related to B by

$$M=B \sin^2 \theta/\lambda^2\,. \tag{1.3}$$

In particular we wish to show how M may be related to thermodynamic quantities with the use of quasi-harmonic lattice theory. In so doing, we also describe the information about lattice vibrations which is obtainable from experimental studies of the Debye–Waller effect. The quasi-harmonic theory provides a completely general and practical way of correlating the different kinds of experimental information without the introduction of detailed models. This point has already been made in part by Blackman (1956), and our paper may be taken as an extension of his.

2. The quasi-harmonic theory

2.1 *The Debye–Waller factors*

The rigorous theory of the Debye–Waller effect has been discussed in detail by other authors (*e.g.* James, 1948). In this section we shall merely state the results that we need for the present paper. Referring to Fig. 1, we can write for the difference in wave vector between reflected and incident radiation

$$\mathbf{Q}=\mathbf{k}_r-\mathbf{k}_i \tag{2.1}$$

where

$$|\mathbf{Q}|=Q=2(2\pi/\lambda)\sin\theta\,. \tag{2.2}$$

In general, there are n different atoms in a primitive cell at positions $\mathbf{r}_\kappa$ ($\kappa=1, 2, \text{---} n$) from a primitive lattice point. We assume that the scattering by each type of atom is determined by a simple atomic scattering factor $f_{0\kappa}(\mathbf{Q})$ and that it is unaffected by the vibrations. It can then be shown, for an ideal mosaic crystal with no extinction, that the ratio of the intensities of the scattered radiation from the vibrating (I) and non-vibrating (I_0) lattice is given by

$$I/I_0=\frac{|\sum_{\kappa=1}^{n} f_{0\kappa}\exp(i\mathbf{Q}\,.\,\mathbf{r}_\kappa)\exp(-M_{\kappa,\mathbf{Q}})|^2}{|\sum_{\kappa=1}^{n} f_{0\kappa}\exp(i\mathbf{Q}\,.\,\mathbf{r}_\kappa)|^2}\,. \tag{2.3}$$

The exponentials exp $(-M_{\kappa,\mathbf{Q}})$ contain the Debye–Waller factors, and for a given reflexion **Q** there is one for each atom κ in a primitive cell.

If anharmonicity of the lattice vibrations can be neglected, $M_{\kappa,\mathbf{Q}}$ depends only on $\langle\{u_{\mathbf{Q}}(\kappa)\}^2\rangle$, the mean square displacement of the atom κ in the direction of **Q**:

$$M_{\kappa,\mathbf{Q}}=8\pi^2 \sin^2\theta/\lambda^2 \langle\{u_{\mathbf{Q}}(\kappa)\}^2\rangle\,. \qquad (2.4)$$

An equivalent but more concise expression can be obtained from equation (2.4) by using equation (2.2):

$$M_{\kappa,\mathbf{Q}}=\tfrac{1}{2}Q^2\langle\{u_{\mathbf{Q}}(\kappa)\}^2\rangle=\tfrac{1}{2}\langle\{\mathbf{Q}\,.\,\mathbf{u}(\kappa)\}^2\rangle\,, \qquad (2.5)$$

while its physical significance can be seen most clearly from a third expression obtained by using the Bragg relation $n\lambda=2d\sin\theta$:

$$M_{\kappa,\mathbf{Q}}=2\pi^2n^2\langle\{u_{\mathbf{Q}}(\kappa)/d\}^2\rangle\,. \qquad (2.6)$$

Thus, according to the quasi-harmonic theory, the Debye–Waller factors depend only on the ratio of the root mean square amplitudes of the atomic vibrations to the spacing of the reflecting planes; conversely, measurements of the temperature dependence of intensities give information about the amplitudes.

2.2 *The Debye–Waller frequency integral*

If the numbers 1, 2, 3 are used to denote any three mutually perpendicular directions in a crystal, it follows from harmonic lattice theory (Blackman, 1956) that

$$\frac{1}{3n}\sum_{\kappa=1}^{n} m_\kappa\langle\{u_1(\kappa)\}^2+\{u_2(\kappa)\}^2+\{u_3(\kappa)\}^2\rangle = \frac{1}{3\mathcal{N}}\int_0^{\omega_m}\frac{G(\omega)\varepsilon(\omega)}{\omega^2}\,d\omega\,. \qquad (2.7)$$

Here, $\mathcal{N}$ is the total number of atoms in the crystal, $G(\omega)d\omega$ is the number of normal modes of vibration with frequencies between ω and $\omega+d\omega$, ω_m is the maximum frequency in the distribution $G(\omega)$, and $\varepsilon(\omega)$ is the mean energy of a normal mode of angular frequency $\omega(=2\pi\nu)$:

$$\varepsilon(\omega)=\tfrac{1}{2}\hbar\omega+\hbar\omega/\{\exp(\hbar\omega/kT)-1\}\,. \qquad (2.8)$$

We call the quantity on the right-hand side of equation (2.7) the *Debye–Waller frequency integral* and denote it by the symbol $X(T)$.

If $M_{\kappa,1}$, $M_{\kappa,2}$, $M_{\kappa,3}$ are the Debye–Waller factors for reflexions from planes perpendicular to the three directions, then from equations (2.5) and (2.7) we have, with an obvious notation (Blackman, 1956):

$$\frac{2}{3n}\sum_{\kappa=1}^{n} m_\kappa\left(\frac{M_{\kappa,1}}{Q_1^2}+\frac{M_{\kappa,2}}{Q_2^2}+\frac{M_{\kappa,3}}{Q_2^3}\right)=X(T)\,. \qquad (2.9)$$

The importance of equation (2.9) is that, whereas the left-hand side relates to the Debye–Waller effect, $X(T)$ depends only on the lattice frequency distribution $G(\omega)$. We shall show in § 3 that $X(T)$ can be derived from experimental thermodynamic data without a knowledge of the detailed shape of $G(\omega)$.

2.3 *Simplification for cubic symmetry*

For the important class of crystals of cubic symmetry, $\langle\{u_{\mathbf{Q}}(\kappa)\}^2\rangle$ is independent of the direction of **Q**; thus

$$M_{\kappa,1}=M_{\kappa,2}=M_{\kappa,3}=M_\kappa\,, \qquad (2.10)$$

and equation (2.9) simplifies to

$$\frac{2}{n}\sum_{\kappa=1}^{n}\frac{m_\kappa M_\kappa}{Q^2}=X(T)\,. \qquad (2.11)$$

The crystals may differ in the numbers and kinds of atom in the primitive cell, and we shall consider three important cases:

(*a*) *Monatomic*, $n=1$ (*e.g. copper, aluminum, etc.*)

Since there is only one type of atom, equation (2.11) becomes simply

$$2mM/Q^2=X(T)\,, \qquad (2.12)$$

and the single Debye–Waller factor M is completely determined by the average over the frequency distribution, $X(T)$.

(*b*) *Monatomic*, $n=2$ (*e.g. diamond, silicon, etc.*)

Although diamond has two atoms in each primitive cell, they are symmetrically equivalent to each other. Thus again there is only one independent Debye–Waller factor:

$$M_1=M_2=M\,. \qquad (2.13)$$

(*c*) *Diatomic*, $n=2$ (*e.g. sodium chloride, zinc sulphide, etc.*)

Here there are two types of atom with different masses (m_1, m_2), atomic scattering factors (f_1, f_2) and Debye–Waller factors (M_1, M_2). Each Bragg reflexion now falls into one of two categories: the reflexions from the two different types of atom are either in phase (summation spectra) or out of phase (difference spectra). The intensity ratios [*cf.* equation (2.3)] are therefore given by

$$(I/I_0)_{\text{sum}}=\frac{|f_1\exp(-M_1)+f_2\exp(-M_2)|^2}{|f_1+f_2|^2}\,, \qquad (2.14)$$

and

$$(I/I_0)_{\text{diff.}}=\frac{|f_1\exp(-M_1)-f_2\exp(-M_2)|^2}{|f_1-f_2|^2}\,. \qquad (2.15)$$

In order to obtain M_1 and M_2 separately, information in addition to that contained in $X(T)$ is required. This might for example be obtained from the ratio of the atomic scattering factors, f_1/f_2.

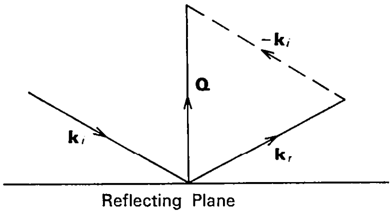

Fig. 1. Simplified wave vector diagram.

3. Determination of $X(T)$

3.1 *Preliminary remarks*

We now consider the Debye–Waller frequency integral and show how it is related to quantities which can also be derived from analyses of thermodynamic data. From experimental heat capacities it is possible to obtain (Barron, Berg & Morrison, 1957; Tosi & Fumi, 1963) moments $\overline{\omega^n}$ of the frequency distribution defined by

$$\overline{\omega^n} = \frac{1}{3\mathcal{N}}\int_0^{\omega_m} \omega^n G(\omega)d\omega \, , \qquad (3.1)$$

for $n > -3$.* Negative moments, *e.g.* $\overline{\omega^{-2}}$ or $\overline{\omega^{-1}}$, can be obtained to about the same accuracy (often $\sim 0{\cdot}2\%$) as the primary experimental data, but higher moments (up to $\overline{\omega^6}$) rather less accurately. In addition, the coefficients in the low frequency expansion for $G(\omega)$ (Blackman, 1937)

$$G(\omega) = \alpha_1\omega^2 + \alpha_2\omega^4 + \alpha_3\omega^6 + \dots \qquad (3.2)$$

may be found. Our aim, therefore, is to express $X(T)$ in terms of moments and the coefficients in equation (3.2).

3.2 *At high temperatures*

At high enough temperatures and neglecting anharmonic effects, $\varepsilon(\omega) = kT$ for each normal mode and $X(T)$ then depends only on $\overline{\omega^{-2}}$ (Blackman, 1956):

$$X(T) = \frac{kT}{3\mathcal{N}}\int_0^{\omega_m} \frac{G(\omega)d\omega}{\omega^2} = kT\overline{\omega^{-2}} \, . \qquad (3.3)$$

The approach to this high temperature limit can be described by a power series in T^{-2} similar to the well-known Thirring expansion for the heat capacity (Barron, Berg & Morrison, 1957). For the energy, we have (Blackman, 1955)

$$\varepsilon(\omega) = kT\left[1 + \sum_{n=1}^{\infty} \frac{B_{2n}\left(\dfrac{\hbar\omega}{kT}\right)^{2n}}{(2n)\,!}\right], \qquad (3.4)$$

and so $X(T)$ becomes

$$X(T) = kT\left[\overline{\omega^{-2}} + \frac{|B_2|}{2\,!}\left(\frac{\hbar}{kT}\right)^2 - \frac{|B_4|}{4\,!}\left(\frac{\hbar}{kT}\right)^4\overline{\omega^2} + \frac{|B_6|}{6\,!}\left(\frac{\hbar}{kT}\right)^6\overline{\omega^4}\dots\right], \qquad (3.5)$$

where the B_{2n} are the Bernoulli numbers

$$(B_2 = \tfrac{1}{6},\ B_4 = -\tfrac{1}{30},\ B_6 = \tfrac{1}{42},\ \dots) \, .$$

This series is absolutely convergent over a wide temperature range ($T > \hbar\omega_m/2\pi k$).

The majority of the measurements of X-ray intensities are made in the temperature region where equation (3.5) is valid. Therefore, in principle, the results may be analysed to yield $\overline{\omega^{-2}}$ and estimates of the first few even moments. In practice, it is found (Barron, Leadbetter, Morrison & Salter, 1963) that experimental incompleteness and uncertainty limit the determination to $\overline{\omega^{-2}}$ (accurate at best to about 1%), but even this may be useful if other kinds of data are not available. On the other hand, good thermodynamic data will give fuller and more accurate information about the moments. The use of the expansion (3.5) will then be to evaluate $X(T)$.

3.3 *At low temperatures*

At $T = 0$ °K, only the zero point energy contributes to $\varepsilon(\omega)$ [equation (2.8)]; $X(T)$ then depends only on $\overline{\omega^{-1}}$:

$$X(0) = \frac{1}{3\mathcal{N}}\int_0^{\omega_m} \frac{\hbar\omega}{2\omega^2}\,G(\omega)d\omega = \tfrac{1}{2}\hbar\overline{\omega^{-1}} \, . \qquad (3.6)$$

Separating the contribution of the zero point energy from that of the thermal energy, we thus obtain for $T > 0$ °K

$$X(T) = \tfrac{1}{2}\hbar\overline{\omega^{-1}} + \frac{1}{3\mathcal{N}}\int_0^{\omega_m} \frac{\hbar}{\omega\{\exp(\hbar\omega/kT) - 1\}}\,G(\omega)d\omega \, . \qquad (3.7)$$

At low temperatures only the low frequency modes contribute appreciably to the integral in equation (3.7), so that the upper limit of integration may be changed to infinity. Substituting the low frequency expansion [equation (3.2)], we obtain

$$X(T) = \tfrac{1}{2}\hbar\overline{\omega^{-1}} + \frac{\hbar}{6\mathcal{N}}\sum_{n=1}^{\infty}\frac{\alpha_n}{2n}|B_{2n}|\left(\frac{2\pi kT}{\hbar}\right)^{2n} \, . \qquad (3.8)$$

Thus $X(T)$ now depends only on $\overline{\omega^{-1}}$ and on the coefficients $\alpha_1, \alpha_2, \alpha_3 \dots$. The corresponding expansion for the heat capacity converges usefully in the approximate range $T < \hbar\omega_m/25k$ (Barron & Morrison, 1957) and a roughly similar range of convergence can be expected for equation (3.8).

The experimental accuracy of X-ray diffraction measurements at low temperatures is such that the results will give at best an estimate of $\overline{\omega^{-1}}$ only. Unless much more accurate measurements can be made in the future, the main use of equation (3.8) will be for the computation of $X(T)$ with values of $\overline{\omega^{-1}}$, α_1, α_2, $\dots$ obtained from thermodynamic data.

3.4 *At intermediate temperatures*

There remains the matter of estimating $X(T)$ in the intermediate temperature range. The necessary information is contained in the thermodynamic data; for example, C_V determines the integral frequency distribution $\int_0^{\omega} G(\omega)d\omega$ quite closely (Barron & Morrison, 1960). A formal relation between $X(T)$ and C_V has been derived by Potapov (1963), but it is not made

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* We are here sliding over the problem of taking explicit account of anharmonic contributions, but this is discussed in the references cited.

clear whether it can be adapted for practical use. In any case, it is much less laborious to interpolate between the high and low temperature expansions and this can be done most easily by using characteristic temperatures. The details will be given in §§ 4.2 and 4.4.

4. Equivalent Debye characteristic temperatures

4.1 *Definitions*

For actual computations, it is convenient to represent measured properties (*e.g.* heat capacity, ratios of intensities of Bragg reflexions *etc.*) by means of equivalent Debye characteristic temperatures. Their merit is that they provide a sensitive way of showing the temperature dependence of the vibrational properties of different crystals, yet the variation in their numerical values stays well within an order of magnitude. Frequently, a 'Θ' is obtained from an experimental Debye–Waller measurement and then compared with a 'Θ' obtained from heat capacity data to see if it 'agrees'. Such a comparison is of little or no value because actual frequency distributions differ from Debye's and because the different experimental properties correspond to different averages over the frequency distribution.

The choice of the Debye distribution as a reference is not arbitrary; it is the simplest distribution which has the two properties common to all crystal distributions: an ω^2 dependence in the limit of vanishingly small frequencies, and the number of modes, $3\mathcal{N}$. When characteristic temperatures are derived from different crystal properties, it is important to distinguish between them (Blackman, 1955). This may be done using a superscript to indicate the property to which a given Θ refers: Θ^C for the heat capacity, Θ^S for the entropy, Θ^M for the Debye–Waller frequency integral, *etc.* The definition of each characteristic temperature is precise and involves no assumptions: $\Theta^P(T)$ represents the observed value of a vibrational property P at the temperature T. Subscripts are used to indicate limiting values at low and high temperatures, *e.g.* Θ_0^P and Θ_∞^P.

The derivation of $\Theta^C(T)$ from heat capacity data is straightforward. Extensive tables are available (Beattie, 1926; Giguère & Boisvert, 1962) which give C_V as a function of Θ/T. It is only necessary to find in the tables the value of Θ/T corresponding to the observed value of C_V and then to multiply it by T to get $\Theta^C(T)$. Since the tables refer to $3N_A$ vibrations, where N_A is Avogadro's number, the experimental molar heat capacities first have to be divided by a factor (*e.g.* 2 for NaCl, 3 for CaF_2 *etc.*) when there are more than $3N_A$ modes per mole.

In a similar way we can determine $\Theta^M(T)$ when X-ray or other measurements yield numerical values of $X(T)$. For a Debye distribution

$$X(T) = \frac{3\hbar^2}{kTx^2}\left\{\frac{x}{4} + \frac{1}{x}\int_0^x \frac{y}{e^y-1}\,dy\right\}, \qquad (4.1)$$

where $x = \hbar\omega_m/kT = \Theta/T$ and $y = \hbar\omega/kT$. A short table of the function $\frac{1}{x}\int_0^x \frac{y}{e^y-1}\,dy$ is given by Debye (1914), and one of the quantity in brackets in equation (4.1) by James (1948; page 219). An extended table for the latter has recently become available (Benson & Gill, 1965).

In several places (*e.g.* James, 1948, page 220; Baldwin & Tompson, 1964), it is remarked that Θ^M should always exceed Θ^C by perhaps a few per cent. The remark is based on an approximate argument presented by Zener & Bilinsky (1936) in which the Debye model is used explicitly. However, the general conclusion is not valid for reasons which will become apparent from subsequent discussion.

4.2 *The $\omega_D(n)$ curve and limiting Debye temperatures*

The moments $\overline{\omega^n}$ occur frequently in the theory of lattice vibrations, and it is convenient to have some way of comparing them with one another. For this purpose, the Debye distribution is again a useful reference. We define the quantity $\omega_D(n)$ as the cut-off frequency of a Debye distribution which has the same nth moment $\overline{\omega^n}$ as the actual frequency distribution of the crystal, so that (Barron, Berg & Morrison, 1957)*

$$\omega_D(n) = \left\{\frac{n+3}{3}\,\overline{\omega^n}\right\}^{1/n}, \quad (n > -3,\ n \neq 0)\,. \qquad (4.2)$$

A graph of $\omega_D(n)$ against n is then a property of the frequency distribution.† Such graphs have been determined from the heat capacities of a number of cubic crystals; two examples whose shapes differ considerably are shown in Fig. 2.

While the $\omega_D(n)$ curves correlate the $\overline{\omega^n}$ with each other, they also allow one to see easily the relative pos-

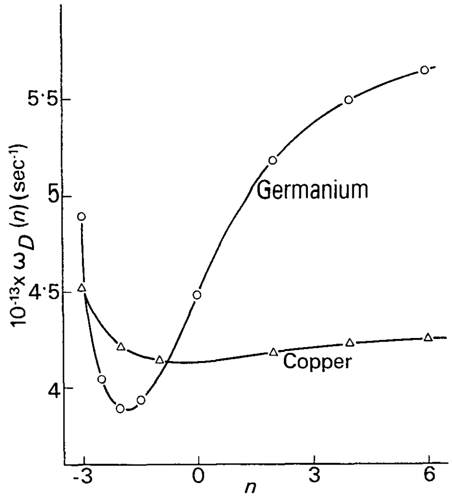

Fig. 2. The function $\omega_D(n)$ against n for germanium and copper.

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* Some authors (*e.g.* Feldman & Horton, 1965) use the corresponding Debye temperatures: $\Theta(n) = \hbar\omega_D(n)/k$.

† Obviously, $\omega_D(n)$ would be a constant for a Debye distribution.

itions of different limiting characteristic temperatures at low and at high temperatures. It has been shown (Barron *et al.*, 1957) that

$$k\Theta_0^C=\hbar\omega_D(-3),\ k\Theta_\infty^C=\hbar\omega_D(2),\ k\Theta_\infty^S=\hbar\omega_D(0)\,, \qquad (4.3)$$

where $\omega_D(-3)$ and $\omega_D(0)$ can be defined as the limits when $n\rightarrow -3$ and $n\rightarrow 0$ of the right-hand side of equation (4.2). In a similar way, the limits for Θ^M are

$$k\Theta_0^M=\hbar\omega_D(-1) \text{ and } k\Theta_\infty^M=\hbar\omega_D(-2)\,. \qquad (4.4)$$

Referring to the curves in Fig. 2, we find that for copper $\Theta_\infty^M>\Theta_\infty^C$ by about 1% while for germanium $\Theta_\infty^C>\Theta_\infty^M$ by about 25%.

4.3 *Expansions for Θ^M*

The high and low temperature expansions for $X(T)$ [equations (3.5) and (3.8)] may be written in terms of characteristic temperatures. For example, if the right hand side of equation (3.8) is equated to the corresponding expression for a Debye distribution with maximum frequency ω_m:

$$X_D(T) = \frac{3\hbar}{4\omega_m}+\frac{3\hbar}{4\omega_m^2}\,|B_2|\left(\frac{2\pi kT}{\hbar}\right)^2, \qquad (4.5)$$

we find

$$\Theta^M(T) = \Theta_0^M\left[1+6{\cdot}580\left\{1-\left(\frac{\Theta_0^M}{\Theta_0^C}\right)^3\right\}\left(\frac{T}{\Theta_0^M}\right)^2+\ldots\right], \qquad (4.6)$$

where numerical values of the constants have been inserted. In a similar way, we obtain for the high temperature region ($T>\hbar\omega_m/2\pi k$):

$$\Theta^M(T) = \Theta_\infty^M\left[1+\frac{1}{7200}\left\{\left(\frac{\Theta_\infty^C}{\Theta_\infty^M}\right)^2-1\right\}\left(\frac{\Theta_\infty^M}{T}\right)^4+\ldots\right] \qquad (4.7)$$

4.4 *Remarks on the temperature dependence of $\Theta^M(T)$*

General knowledge of the $\omega_D(n)$ curves of different crystals can be used to arrive at some fairly definite conclusions about the probable temperature dependence of $\Theta^M(T)$. In the first place, $\omega_D(n)$ usually has a minimum between $n=0$ and $n=-3$, and often between $n=-1$ and $n=-2$ (*e.g.* germanium, Fig. 2). This means that Θ_0^M and Θ_∞^M [equation (4.4)] are unlikely to differ by more than about 10%; usually they will differ by much less.

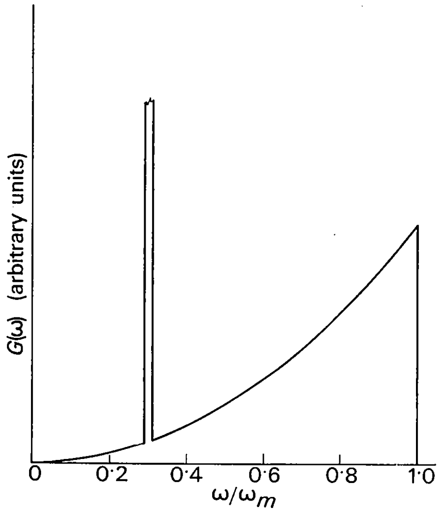

Fig. 3. The frequency distribution for the theoretical example (§4·5).

In the second place, there is no term in T^{-2} in equation (4.7), so that we may expect $\Theta^M(T)$ to remain approximately constant down to lower temperatures than does $\Theta^C(T)$. If we take $\Theta_\infty^C/\Theta_\infty^M\sim 1{\cdot}25$ (a large value, as in the example of germanium), the second term of equation (4.7) contributes less than 1% in the region $T>\Theta_\infty^C/3$. It thus appears that the typical variation of $\Theta^M(T)$ is likely to be much less than that of $\Theta^C(T)$ and that even a crude assumption that $\Theta^M(T)$ is a constant may often be quite a good approximation. If required, the detailed behaviour of $\Theta^M(T)$ between the ranges of convergence of equations (4.6) and (4.7) can be determined using Padé approximants (Salter, 1965).

These conclusions apply only to a typical vibrational distribution. They do not necessarily apply to distributions which have large parts widely separated in frequency. Such distributions are found in layer structures, where frequencies for motion perpendicular to the planes are lower than for motion within the planes. Molecular crystals provide another example: the frequencies of internal vibrations are commonly much higher than those of 'translation' or 'libration'. For such crystals, it will usually be more appropriate to consider the different kinds of frequencies separately rather than to lump them together in a single $X(T)$ (Leadbetter, 1965).

4.5 *A theoretical example*

To illustrate the deductions made above, we compute characteristic temperatures for a simple model distribution in which $\frac{9}{4}\mathscr{N}$ normal modes are in a Debye distribution with cut-off ω_m and $\frac{3}{4}\mathscr{N}$ in a monochromatic peak at $\omega=0{\cdot}3\omega_m$ (Fig. 3). This distribution has most of the properties of a typical distribution (but no dispersion at low frequencies) and is amenable to computation. The $\omega_D(n)$ and $\Theta^M(T)$ curves are remarkably similar to those estimated by Feldman & Horton (1963) for white tin.

The $\omega_D(n)$ curve is shown in Fig. 4. From it, we conclude that there should be a marked variation in $\Theta^C(T)$, with $\Theta_0^C>\Theta_\infty^C$, but very little variation in $\Theta^M(T)$. This is confirmed by the computed $\Theta(T)$ curves shown in Fig. 5. The very flat initial portion of the $\Theta^C(T)$ curve is due to the absence of dispersion; for real crystals, $\Theta^C(T)$ and $\Theta^M(T)$ will usually show parabolic temperature dependences in opposite directions at low temperatures. A rather similar illustration of the variation of $\Theta^M(T)$ and $\Theta^C(T)$ with temperature is provided by curves calculated by Batterman & Chipman (1962) for germanium from a frequency distribution derived by Phillips (1959). Both of these examples show that the simple generalization of Zener & Bilinsky (1936) that $\Theta^M(T) > \Theta^C(T)$ cannot be maintained.

5. Practical computations

5.1 *The volume dependence of* $\Theta^M(T)$

The results we have discussed so far apply only to a fixed volume, whereas in practice the volume of a crystal changes with temperature. We can allow for thermal expansion and also calculate the pressure dependence of the vibrational properties, if we know the volume dependence of the frequency distribution. Paskin (1957) has suggested the use of the Grüneisen parameter γ, which he defines as $-d \ln \theta / d \ln V$; but it is necessary to be more precise here because Θ is not unique. Since the total volume change due to thermal expansion is usually very small below $\Theta/3$, it will normally suffice to know the volume dependence of Θ^M_∞. From the second part of equation (4.4) we obtain

$$\gamma(-2) = -\frac{d \ln \omega_D(-2)}{d \ln V} = -\frac{d \ln \Theta^M_\infty}{d \ln V}, \quad (5.1)$$

where $\gamma(n)$ is defined by (Barron, 1955)

$$\gamma(n) = -\frac{1}{n} \frac{d \ln \overline{\omega^n}}{d \ln V}. \quad (5.2)$$

Therefore to bring values of $\Theta^M(T)$ to the basis of a single volume V_0, we may use

$$\frac{\Theta^M(V_0)}{\Theta^M(V)} = \left(\frac{V}{V_0}\right)^{\gamma(-2)}. \quad (5.3)$$

It is shown elsewhere (Barron, Leadbetter & Morrison, 1964) that $\gamma(n)$ curves can be calculated from the thermal expansion in much the same way that $\omega_D(n)$ curves can be calculated from the heat capacity. In particular, $\gamma(-1)$ and $\gamma(-2)$ can be obtained to within a few per cent if accurate thermal expansion data are available down to low temperatures.

5.2 *The inverse second moment*

From the point of view of coherent scattering measurements, the most useful quantity which can be derived from thermodynamic results is the inverse second moment, $\overline{\omega^{-2}}$. This is because numerical values of $X(T)$ or $\Theta^M(T)$ will usually be wanted in the high temperature region. We therefore outline a simple graphical procedure for obtaining $\overline{\omega^{-2}}$ from heat capacity data.

The general relation between the harmonic heat capacity and the negative moments is (Barron, Berg & Morrison, 1957)

$$\frac{1}{3\mathcal{N}k} \int_0^T \frac{C(\tau)}{\tau^n} d\tau = \Gamma(n+1)\zeta(n)\overline{\omega^{1-n}} \left(\frac{\hbar}{k}\right)^{1-n}$$
$$- \frac{1}{(n-1)} \frac{1}{T^{n-1}} + \sum_{s=1}^{\infty} (-1)^{s+1} \frac{|B_{2s}|}{(2s)!}$$
$$\times \frac{(2s-1)}{(2s+n-1)} \frac{\omega^{2s}}{T^{2s+n-1}} \left(\frac{\hbar}{k}\right)^{2s}, \quad (5\cdot4)$$

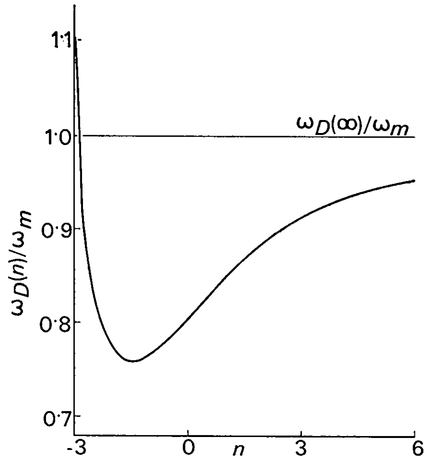

Fig. 4. The function $\omega_D(n)$ against n for the theoretical example (§4·5).

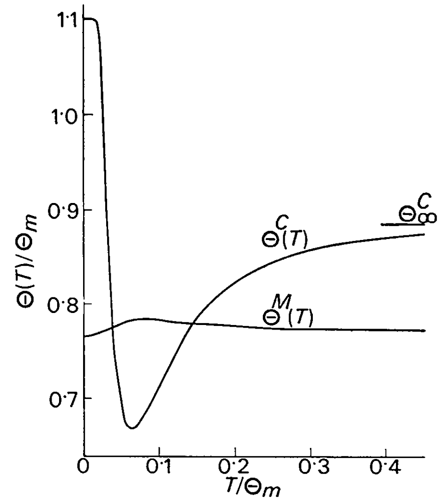

Fig. 5. The temperature dependence of the characteristic temperatures $\Theta^M(T)$ and $\Theta^C(T)$ for the theoretical example. ($\Theta_m = \hbar\omega_m/k$).

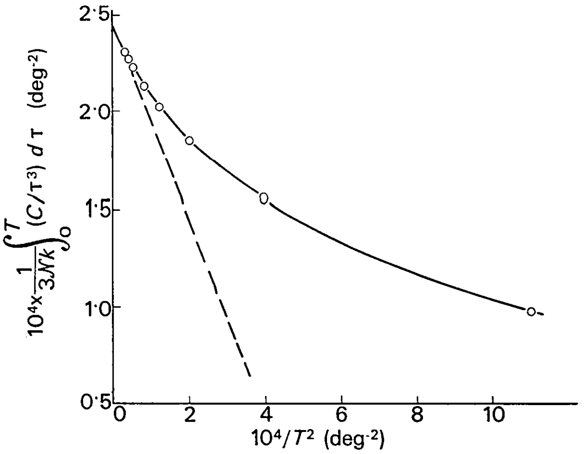

Fig. 6. The graphical determination of the inverse second moment of the frequency distribution of germanium.
- - - - line of limiting slope.

where $1<n<4$, $\Gamma(n+1)$ is the gamma function and $\zeta(n)$ the Riemann zeta function (both tabulated by Jahnke & Emde, 1945). With $n=3$, the inverse second moment is therefore given by

$$\frac{1}{3\mathcal{N}k}\int_0^T \frac{C(\tau)}{\tau^3}\,d\tau = 7{\cdot}212\,\overline{\omega^{-2}}\left(\frac{\hbar}{k}\right)^{-2} - \frac{1}{2T^2} + \frac{1}{48}\,\frac{\overline{\omega^2}}{T^4}\left(\frac{\hbar}{k}\right)^{2} - \dots \qquad (5{\cdot}5)$$

If the integral on the left-hand side of equation (5·5) is plotted against $1/T^2$, the graph should be a curve with an intercept of $7{\cdot}212\,\overline{\omega^{-2}}\,(\hbar/k)^{-2}$ and limiting slope of $-\frac{1}{2}$ at $1/T^2=0$. Fig. 6 shows such a graph for data for germanium in the region $30° < T < 180$ °K (*i.e.* $12 > \theta_0^C/T > 2$), giving $\theta_\infty^M = 297$ °K. If required, $\overline{\omega^{-1}}$ and θ_0^M can be obtained by taking $n=2$ in equation (5·4); the initial coefficient $\zeta_{(2)}\Gamma_{(3)} = 3{\cdot}290$.

The example of germanium is a particularly favourable one because the expansivity of the crystal is small and because there is no ambiguity about the number of vibrations [*i.e.* about $\mathcal{N}$ in equation (5·5)]. Thus, in order to obtain $\overline{\omega^{-2}}$ to within a few tenths of a percent, either C_p or C at a fixed volume may be used in the plot such as Fig. 6. For other substances, *e.g.* for molecular crystals, the accuracy with which $\overline{\omega^{-2}}$ can be determined will be less but, as a rough rule, should not usually be worse than about 2% even when only crude corrections for expansivity can be made.

6. Constant volume anharmonic effects

Throughout this paper, the only anharmonic effects considered have been those due to thermal expansion. There are additional anharmonic corrections to the temperature factor that occur even when the crystal is held at constant volume (Maradudin & Flynn, 1963), but these cannot be estimated from purely thermodynamic measurements without additional assumptions. They will in general be of the same order of magnitude (but not necessarily of the same sign) as the corrections due to thermal expansion. They will not therefore affect seriously the results and conclusions of this paper except at high temperatures, where accurate measurements of the temperature factor can in principle give information about the lattice vibrations unobtainable from thermodynamic properties.

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